# PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

## Causing Colour Changes in Polymer Plastics by Irradiation

We, T.I. (GROUP SERVICES) LIMITED, a British Company, of Rocky Lane, Aston, Birmingham 6, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the decoration, printing and colouration of polymer plastics, in particular those that contain chlorine as a constituent element.

Plastics in general have inert impervious surfaces and do not lend themselves to printing by normal means. Special printing media, embossing devices and colouring processes have been exploited to overcome this limitation, yet despite the increased costs and decreased throughput rate which are necessarily involved, the resultant imprints are stil not completely durable.

It is now proposed, according to the present invention, to produce colour changes penetrating the surfaces of polymer plastics of which the monomer contains chlorine as a constituent element by exposing the surface of the plastic to the action of high energy ionising radiation such as X-rays, alpha particles, gamma rays, and high energy electrons. By exposing only selected areas of the surface, coloured patterns may be produced. It has been found that such plastics undergo colour changes when exposed to high energy radiation and this property may be made use of to produce completely durable and permanent imprints on the plastics in the form of sheets, films, coatings on other materials, plastic-impregnated paper, filaments and woven fibres. The invention is found to be particularly applicable to polyvinyl chloride, polyvinylidene chloride, rubber hydrochloride (which is based on a naturally occurring polymer), and in general solid polymers and copolymers of unsaturated chlorohydrocarbons, in as much as these polymers are particularly sensitive to high energy radiation.

In contrast with superficial patterns produced by normal means, the patterns produced by high energy radiation go through the thickness of the material when it is sheets or plates, creating an inverted replica on the further surface. This novel feature arises because the plastic material which may be opaque to visible light is none the less transparent to high energy radiation. Such surface properties as roughness, porosity, wetting power, uniformity are of no consequence, as articles may be printed without any physical contact with the surface. In many cases, the plastic material may be printed without needing to remove protective wrapping. Similarly, multiple printing or patterning is possible by irradiating a stack or pile of films or sheets. In practice therefore printing patterns on surfaces can be performed without needing to separate the surfaces.

Such a process is important not only in permitting a large number of sheets to be printed at the same time, which allows a high throughput rate, but also affording exact register. Handling charges are reduced since the plastic material can be decorated in certain cases without removal from the roll or wrapping in which it is delivered.

Many other applications of this invention can be visualised. The equivalent to inlaid linoleum could be produced without use of the inlaying process, and the pattern would be completely durable. Shower curtains can be printed on the roll or in multiple stacks. The pattern will be equal on both sides. Plastic shoe soles, and upholstery materials could be imprinted with a design or a manufacturer's identification mark, which would never wear out as long as the material lasts. Buttons could be stamped out of polyvinyl chloride sheets and then rumbler-polished

without danger of removing the design. Cable coverings can be identified by printing on the coil. Irregular surfaces can be decorated or printed as readily as smooth surfaces.

A suitable source of radiation, though by no means the only possible one, is an electron accelerator of the Van de Graaff type. The radiation dosage is easily controlled and the beam of electrons is in a conveniently concentrated and directed form.

The use of lead or similar stencils is by no means obligatory. It is possible to produce patterns by the manipulation of the electron beam as in a television receiver. This would be more economical in irradiation time and would enable various shades to be obtained so that a photographic effect could be produced within the material.

Another use of the invention is for indicating by the colour change produced, the dose of radiation which an article has received. Irradiation from high energy electrons and like sources is used to produce physical and chemical changes in certain materials, and it may also be used for the preservation of foodstuffs. Often the changes brought about by the irradiation produce no outwardly visible or tactile effects, and it is difficult to ensure that an irradiated article has received the correct dose, or a dose that is uniformly distributed. Where batches of articles are to be irradiated on a production basis it is normally impossible to check that none of them have been missed.

It is now proposed to attach to or include with each article before irradiation a tab, tape, or the like of a material which undergoes a colour change on irradiation. Then a glance will tell whether all the articles of a batch have received their proper dose. An adhesive tape of the sensitive material passed round an article will indicate whether all sides of it have been dosed equally. The indicator may also be used as a rough gauge to estimate the magnitude of a dose according to the degree of colour change observed.

For this last-mentioned purpose, that of gauging the dose that has been received, it is not essential that the colour change should be permanent, and one could use an irradiation-induced colour-change which is known to disappear in time.

The invention will now be described more fully with reference to certain examples.

### Example I

A number of samples of the vinyl chloride homopolymer sold by I.C.I. Limited under the Registered Trade Mark "Darvic" were exposed to varying doses of radiation by high energy electrons from a 2 MeV Van de Graaff accelerator. The following table shows the dose received in each case, the initial starting colour, and the final colour; the samples were opaque and contained various colour pigments. The samples are identified by arbitrary formula numbers.

| Formula No. | Initial Colour | Dose (Mrad) | Final Colour | |
|---|---|---|---|---|
| 110 | Natural (i.e. unpigmented) | 2.5 | Deep amber | A |
| 410 | Red | 4.5 | Dark red | B |
| 770 | Pale blue | 4.5 | Grey | B |
| 015 | Blue white | 4.5 | Yellow | B |
| 010 | White | 4.5 | Slight yellow | B |
| 225 | Yellow | 7.5 | Mustard | B |
| 446 | Pink | 16.5 | Brown | B |
| 550 | Brown | 16.5 | Dark brown | B |
| 115 | Cream | 16.5 | Beige | B |
| 661 | Pale green | 16.5 | Grey-green | B |

A signifies marked change
B signifies moderate change

By placing a mask of electron absorbing material such as lead over selected areas of the sample, it was possible to obtain any desired pattern of colour.

### Example II

A number of samples of the vinyl chloride-vinylidene chloride co-polymer sold by BX Plastics Limited under the Registered Trade

Mark "Cobex" were exposed to varying doses of radiation by high energy electrons from a 2 MeV Van de Graaff accelerator. The following table shows the results; the samples were opaque and contained various pigments. In the table the different samples are identified by arbitrary formula numbers.

| Formula No. | Initial Colour | Dose (Mrad) | Final Colour | |
|---|---|---|---|---|
| 5046 | Pale blue | 2.5 | Grey | B |
| 5023 | Orange | 2.5 | Mustard | B |
| 5036 | Apple green | 2.5 | Grey-green | A |
| 5031 | Green | 6.5 | Dark green | B |
| 5072 | Cream | 6.5 | Dark yellow | B |
| 5073 | Cream | 6.5 | Grey | B |
| 5043 | Pale blue | 6.5 | Grey | B |
| 5004 | Pink | 6.5 | Grey | A |
| 5016 | Pink | 6.5 | Grey | A |
| 5065 | White | 6.5 | Grey | A |
| 5098 | Grey | 15.5 | Dark grey | B |
| 5025 | Yellow | 15.5 | Stone | A |
| 5095 | Grey brown | 15.5 | Dark grey | A |
| 5047 | Blue | 15.5 | Grey | A |
| 5001 | Beige | 15.5 | Maroon | B |
| 5112 | Brown | 15.5 | Red-brown | B |
| 5049 | Brown | 15.5 | Red-brown | B |

A signifies marked change
B signifies moderate change

Examination of "Cobex" samples immediately after irradiation showed that two types of colour effect are present together. One effect is a transient one due to electron trapping or trapped free radicals and with "Cobex" shows as a blue tinge in the material, independent of the original colour: the other effect is caused by a decomposition of the base material not unlike that produced by prolonged exposure to strong ultraviolet light. Several irradiated originally white samples have been heated for a few minutes in an oven at 120°. The blue colour did not diminish appreciably, but the base material darkened further. The effect of ultraviolet light of wavelength 2537 Å on an irradiated "Cobex" sample was to cause the blue colour to disappear. This can be explained by the release of trapped electrons from a metastable position. At the same time ultraviolet light produces a further effect on the base material so that subsequent heating caused it to darken much more than samples which had been irradiated with electrons, but had not been subjected to ultraviolet light. Samples which are exposed to daylight or artificial light lose their blue tinge after a few weeks, but the darkening of the base material persists, and presumably would tend to become more marked with time. This increased darkening at room temperature has not been noted in our qualitative experiments with "Cobex," but several different coloured transparent samples of the plasticised polyvinyl chloride sold by I.C.I. Limited under the Registered Trade Mark "Welvic," which showed only a moderate darkening on irradiation with 14 Mrad, had become an almost opaque maroon after three months.

The colour changes with plastics containing polyvinyl chloride are dependent on the other components of the material. That the colorant itself has an effect was established by measurements on different coloured samples of trans-

parent "Cobex." These were uniformly electron-irradiated with 5 Mrad, when each acquired a more intense colour. The difference spectra (indicating the superimposed colour) of the samples before and after irradiation were then recorded using a Beckmann DK2 Recording Spectrophotometer over the visible band 4000—7000 Å. If the colorant were without effect, the difference spectra would have been the same for all the specimens. It was found, however, that the difference spectra altered from sample to sample both with respect to the location of the peaks and the magnitude of the absorption, and that the presence of a colorant always increases the colour change in comparison with natural (i.e. unpigmented) "Cobex."

EXAMPLE III

Selected areas of a film sample of plasticised polyvinyl chloride of the kind sold by BX Plastics Limited under the Registered Trade Mark "Velbex" was irradiated with a dose of 10 Magarade by electrons from a 2 MeV Van de Graaff accelerator. The test was repeated with films of various colours. An uncoloured sample showed a slight yellowing and most of the coloured samples showed a bleaching. A dark green sample known as "Privet Green" 561/0996 changed to dark blue. Heating at 120° for two hours caused no change either in the original colour or in the irradiation-produecd colour, and overnight exposure to light of wavelength 2537 Å produced no effect except a slight extra bleaching of some of the irradiated samples. These results contrast with those obtained on "Cobex" and are unexpected as it is known that the manufacture of rigid polyvinyl chloride compositions requires higher processing temperatures than plasticised materials and consequently it would appear necessary to include more efficient or larger amounts of heat stabilisers in rigid compositions. Such inclusions should stabilise the materials to a great extent during irradiation or subsequent exposure to heat. The reverse was actually observed, the colour of these plasticised compositions being more stable both to radiation and to subsequent heat treatment.

EXAMPLE IV

This is an example of a colour change which could be used as an indication of radiation dosage. One of the samples of polyvinyl chloride mentioned earlier is included with a material which is to be irradiated but which undergoes no visible change on irradiation. The polyvinyl chloride undergoes a known colour change with a given dose of radiation; it could be made up in the form of tape or tags. Tags of polyvinyl chloride can be placed inside pharmaceutical and medical-dressing packs which are to be sterilised by irradiation. The consumer can then examine the colour of the tag and thus check whether the material has received adequate radiation.

WHAT WE CLAIM IS:—

1. A method of producing colour changes penetrating the surfaces of polymer plastics of which the monomer contains chlorine as a constituent element comprising exposing areas of the surface of the plastic to the action of high energy ionising radiation such as X-rays, alpha particles, gamma rays, and high energy electrons.

2. A method of producing colour changes according to Claim 1, as applied to a polymer or copolymer of an unsaturated olefinic chlorohydrocarbon.

3. A method of producing colour changes according to Claim 2, as applied to a polyvinyl chloride or polyvinylidene chloride polymer or a copolymer of these.

4. A method of producing colour changes according to Claim 2, as applied to rubber hydrochloride.

5. A method of producing colour changes according to Claim 1 or Claim 2, in which the radiation comprises high energy electrons from an electron accelerator.

6. Patterned polymer plastic sheets, films, coatings on other materials, plastic impregnated paper, filaments, woven fibres and the like, in which the pattern is produced by subjecting selected areas of the surface of the material to the process according to any of the preceding claims.

7. A method of testing applicable to the manufacture of irradiated materials by exposing them to selected doses of high energy ionising radiation, the method comprising the inclusion, adjacent to the material to be irradiated, and in the path of the beam of high energy radiation to be used, of a piece of polymer plastic of which the monomer contains chlorine as a constituent element and which is of a kind which undergoes a visible colour change on exposure to high energy radiation of substantially the selected dose.

8. A method of testing according to Claim 7, in which the polymer plastic is a polymer of an unsaturated olefinic chlorohydrocarbon.

9. A method of producing colour changes according to Claim 1, substantially as described with reference to any one of the accompanying examples.

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# PROVISIONAL SPECIFICATION

No. 22494 A.D. 1956

## Causing Colour Changes in Polymer Plastics by Irradiation

We, T.I. (GROUP SERVICES) LIMITED, a British Company, of Rocky Lane, Aston, Birmingham 6, do hereby declare this invention to be described in the following statement:—

This invention relates to the decoration, printing or colouration of plastic materials and in particular those that contain chlorine as a constituent element.

Plastic materials in general have inert, impervious surfaces and do not lend themselves to printing by normal means. Special printing media, embossing devices and colouring processes have been exploited to overcome this limitation, yet despite the increased costs and decreased throughput rate which are necessarily involved, the resultant imprints are still not completely durable. It has now been found, according to the present invention, that completely durable and permanent imprints or patterns can be produced on plastic sheets, films, coatings and plastic coated or impregnated paper, filaments and woven fibres by subjecting them, through suitable stencils, to high energy radiations such as X-rays. $\alpha$-rays, high energy electrons and the like. It is further found that the process is particularly effective if applied to plastic materials containing chlorine as a constituent element, such as polyvinyl chloride, polyvinylidene chloride, rubber hydrochloride, and in general solid polymers and copolymers of unsaturated chlorohydrocarbons, in as much as these polymers are particularly sensitive to high energy radiation.

In contrast with superficial patterns produced by normal means, the patterns produced by high energy radiation go through the thicknes of the material when it is sheets or plates, creating an inverted replica on the further surface. This novel feature arises because the plastic material which may be opaque to visible light is none the less transparent to high energy radiation. In practice therefore printing patterns on surfaces can be performed without needing to separate the surfaces, in short, multiple printing or patterning is possible by irradiating a stack or pile of films or sheets.

Such a process is important not only in permitting a large number of sheets to be printed at the same time, which allows a high throughput rate, but also affording exact register. Handling charges are reduced since the plastic material can be decorated in certain cases without removal from the roll or wrapping in which delivered.

Broadly speaking, the process comprises compounding polyvinyl chloride or similar polymer with a suitable stable pigment preferably of light shade and with plasticisers, fillers, stabilisers and lubricants as desired according to the usual art, and converting the compound into the desired final form. A suitable stencil is now overlaid upon a stack or roll and the plastic material and the assembly is subjected to high energy radiation. The material construction of the stencil is variable depending on the penetrating power of the radiations. Thus thick lead may be necessary to stop hard X- or $\gamma$-rays but the imprint of a lead pencil may be sufficient for a pure $\alpha$-particle emitter. Using $\alpha$-particles, the radiation induced pattern may not extend beyond the surface of the plastic film or coating, but this would be of use as a duplicating process, that can be performed without protection of the paper from light at any stage.

Many other applications of this invention can be visualised. The equivalent to inlaid linoleum could be produced without use of the inlaying process, and the pattern would be completely durable. Shower curtains can be printed on the roll or in multiple stacks. The pattern will be equal on both sides. Plastic shoe soles, and upholstery materials could be imprinted with a design or a manufacture's identification mark, and would never wear out as long as the material lasts. Buttons could be stamped out of p.v.c. sheets and then rumbler-polished without danger of removing the design. Cable coverings can be identified by printing on the coil. Irregular surfaces can be decorated or printed as readily as smooth surfaces.

The articles which can be decorated in this way are preferably made from a polymer containing chlorine as a constituent element, but this polymer may be present as only a small portion of the total assembly as e.g. in plastic coated fabrics such as Vynide or as impregnated paper.

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# PROVISIONAL SPECIFICATION

No. 12681 A.D. 1957

## Causing Colour Changes in Polymer Plastics by Irradiation

We, T.I. (GROUP SERVICES) LIMITED, a British Company, of Rocky Lane, Aston, Birmingham 6, do hereby declare this invention to be described in the following statement:—

This invention relates to the irradiation of materials by means of high energy radiation such as X-rays, gamma rays, high energy electrons and the like.

Such irradiation is known to produce physical and chemical changes in certain materials, in particular polymer plastics and rubbers, and it may also be used for the preservation of foodstuffs. Often the changes brought about by the irradiation produce no outwardly visible or tactile effects, and it is difficult to ensure that an irradiated article has received the correct dose, or a dose that is uniformly distributed. Where batches of articles are to be irradiated on a production basis it is normally impossible to check that none of them have been missed.

According to the invention it is proposed to attach to or include with each article before irradiation a tab, tape, or the like of a material which undergoes a colour change on irradiation. Then a glance will tell whether all the articles of a batch have received their proper dose. An adhesive tape of the sensitive material passed around an article will indicate whether all sides of it have been dosed equally. The indicator may also be used as a rough gauge to estimate the magnitude of a dose according to the degree of colour change observed.

Particularly suitable materials for the purpose are chlorinated polymers such as polyvinyl chloride or a vinyl chloride-vinylidene chloride copolymer, with or without a colouring pigment or dye. The materials in clear form, without any pigment or dye, will generally show a yellow colouration on irradiation and the coloured materials will show various changes depending on the starting colour.

Materials other than chlorinated polymers may be used for the indicator. For example, nylon, polymethyl methacrylate, and thermosetting resins such as ureaformaldehyde may be suitable, provided that certain suitable colourants are present.

The material is conveniently made up in the form of an adhesive tag, or as a continuous pressure-sensitive tape from which pieces may be detached and applied to the article. For packaged foodstuffs which are to be irradiated to preserve them, a tab of sensitive material may be included in each package before irradiation.

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